



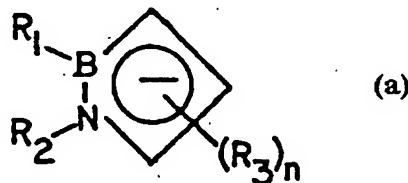
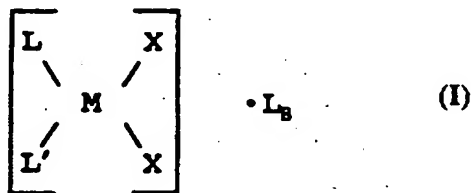
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(21) International Application Number: PCT/US96/03665 (22) International Filing Date: 18 March 1996 (18.03.96) (30) Priority Data: 08/428,384 25 April 1995 (25.04.95) US (71) Applicant: OCCIDENTAL CHEMICAL CORPORATION [US/US]; 360 Rainbow Boulevard South, Niagara Falls, NY 14303 (US). (72) Inventors: NAGY, Sandor, 2159 B Bedell Road, Grand Island, NY 14072 (US). KRISHNAMURTI, Ramesh; 121 Pepper Tree Road, Amherst, NY 14228 (US). ETHERTON, Bradley, P.; 11827 Orchard Mountain Drive, Houston, TX 77059 (US). (74) Agents: FUERLE, Richard, D. et al.; Occidental Chemical Corporation, 360 Rainbow Boulevard South, Niagara Falls, NY 14303 (US).		(81) Designated States: AL, AM, AU, AZ, BB, BG, BR, BY, CA, CN, CZ, EE, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. With amended claims.	

(54) Title: AZABOROLINYL METAL COMPLEXES AS OLEFIN POLYMERIZATION CATALYSTS

(57) Abstract

Disclosed is a catalyst having general formula (I) where L is a ligand having formula (a). L' is L, Cp, Cp*, indenyl, fluorenyl, NR₂, OR, or halogen, L can be bridged to L'; X is halogen, NR₂, OR, or alkyl from C₁ to C₁₂, M is zirconium or hafnium, R is alkyl from C₁ to C₁₂ or aryl from C₆ to C₁₂, R₁ is R, alkaryl from C₆ to C₁₂, aralkyl from C₆ to C₁₂, hydrogen, or Si(R)₃, R₂ is R₁, halogen, COR, COOR, SOR, or SOOR, R₃ is R₂, OR, N(R)₂, SR, or a fused ring system, Cp is cyclopentadienyl, Cp* is pentamethylcyclopentadienyl, n is 0 to 3, and L₈ is an optional Lewis base. Also disclosed is a method of making a poly-α-olefin comprising polymerizing an α-olefin monomer using a catalyst such as that described above where M can be titanium, zirconium, or hafnium.



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5 AZABOROLINYL METAL COMPLEXES AS
 OLEFIN POLYMERIZATION CATALYSTS

Background of the Invention

 This invention relates to catalysts useful in homo- and
 co-polymerizing ethylene and other olefinic hydrocarbons. In
10 particular, it relates to catalysts containing a transition
 metal π -bonded to a ligand that contains an azaboroline ring.

 Until recently, polyolefins have been primarily made with
 conventional Ziegler catalyst systems. These catalysts
 typically consist of transition metal-containing compounds and
15 one or more organometallic compound. For example,
 polyethylene has been made using Ziegler catalysts such as
 titanium trichloride and diethylaluminum chloride, or a
 mixture of titanium tetrachloride, vanadium oxytrichloride,
 and triethylaluminum. These catalysts are inexpensive but
20 they have low activity and therefore must be used at high
 concentrations. As a result, it is sometimes necessary to
 remove catalyst residues from the polymer, which adds to
 production costs. Neutralizing agents and stabilizers must be
 added to the polymer to overcome the deleterious effects of
25 the catalyst residues. Failure to remove catalyst residues
 leads to polymers having a yellow or grey color and poor
 ultraviolet and long term stability. For example, chloride-

containing residues can cause corrosion in polymer processing equipment. Furthermore, Ziegler catalysts produce polymers having a broad molecular weight distribution, which is undesirable for some applications such as injection molding. They are also poor at incorporating α -olefin co-monomers. Poor co-monomer incorporation makes it difficult to control the polymer density. Large quantities of excess co-monomer may be required to achieve a certain density and many higher α -olefins, such as 1-octene, may be incorporated at only very low levels, if at all.

Although substantial improvements in Ziegler catalyst systems have occurred since their discovery, these catalysts are now being replaced with the recently discovered metallocene catalyst systems. A metallocene catalyst typically consists of a transition metal compound which has one or more cyclopentadienyl ring ligands. They have low activities when used with organometallic compounds, such as aluminum alkyls, which are used with traditional Ziegler catalysts, but very high activities when used with aluminoxanes as cocatalysts. The activities are generally so high that catalyst residues need not be removed from the polymer. Furthermore, they produce polymers with high molecular weights and narrow molecular weight distributions. They also incorporate α -olefin co-monomers well. However, at higher temperatures metallocene catalysts tend to produce

lower molecular weight polymers. Thus, they are useful for gas phase and slurry polymerizations of ethylene, which are conducted at about 80°C to about 95°C, but they do not generally work well in solution polymerizations of ethylene, at about 150°C to about 250°C. The polymerization of ethylene in solution is desirable because it allows great flexibility for producing polymers over a wide range of molecular weights and densities as well as the use of a large variety of different co-monomers. One can produce polymers that are useful in many different applications. For example, high molecular weight, high density polyethylene (PE) film useful as a barrier film for food packaging and low density ethylene co-polymers with good toughness and high impact strength.

Summary of the Invention

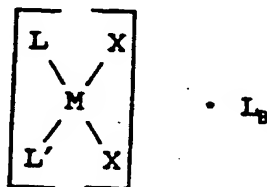
We have found a new class of catalysts based on an azaboroline ring structure and containing a transition metal. The catalysts of this invention have unusually high activities, which means that they can be used in very small quantities. They are also very good at incorporating co-monomers into the polymer. They have good activity at higher temperatures and are therefore expected to be useful in solution polymerizations of ethylene.

We have also discovered that the hydrogen response of monomers polymerized with the catalysts of this invention is

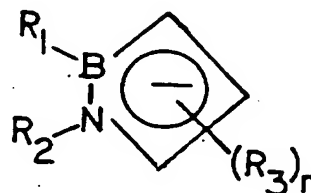
better than with other catalysts. That is, when the catalysts of this invention are used to polymerize monomers, small variations in the amount of hydrogen present have a large effect on the molecular weight of the resulting polymer.

Description of the Preferred Embodiments

The catalysts of this invention have the general formula

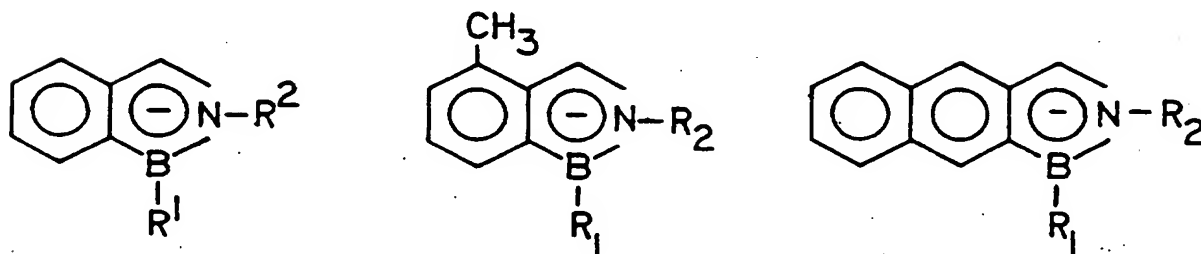


where L is a ligand having the formula



L' is L, Cp, Cp', indenyl, fluorenyl, NR₂, OR, or halogen, L can be bridged to L', X is halogen, NR₂, OR, or alkyl from C₁ to C₁₂, M is titanium, zirconium, or hafnium, R is alkyl from C₁ to C₁₂ or aryl from C₆ to C₁₂, R₁ is R, alkaryl from C₆ to C₁₂, aralkyl from C₆ to C₁₂, hydrogen, or Si(R)₃, R₂ is R₁, halogen, COR, COOR, SOR, or SOOR, R₃ is R₂, OR, N(R)₂, SR, or a fused ring system, Cp is cyclopentadienyl, and Cp' is pentamethylcyclopentadienyl.

The L' ligand is preferably Cp, Cp*, or L as those compounds are easy to make and have good activity. The X group is preferably halogen and most preferably chlorine as those compounds are more readily available. The R group is preferably alkyl from C₁ to C₄, the R₁ group is preferably alkyl from C₃ to C₁₂ or aryl, the R₂ group is preferably t-butyl or trimethylsilyl, and the R₃ group is preferably hydrogen or methyl as those compounds are easier to make. Examples of fused ring structures that can be used for R₃ include

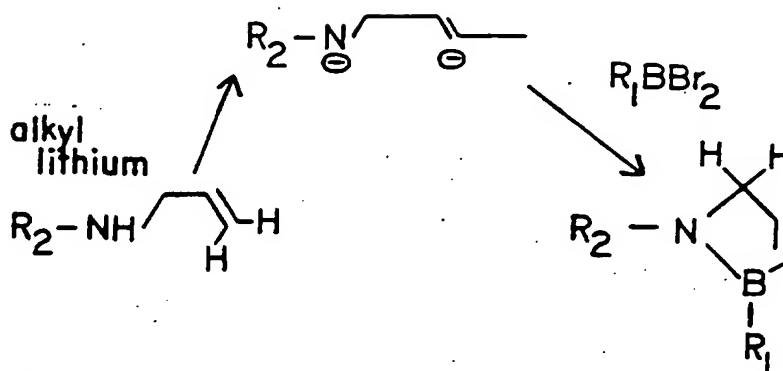


The metal M is preferably zirconium, as the zirconium catalysts offer a good combination of activity and stability.

Optionally, L can be bridged to L'. Groups that can be used to bridge the two ligands include methylene, ethylene, 1,2-phenylene, dimethylsilyl, diphenylsilyl, diethylsilyl, and methylphenylsilyl. Normally, only a single bridge is used in a catalyst. It is believed that bridging the ligands changes the geometry around the catalytically active transition metal and improves the catalyst activity and other properties, such as comonomer incorporation and thermal stability.

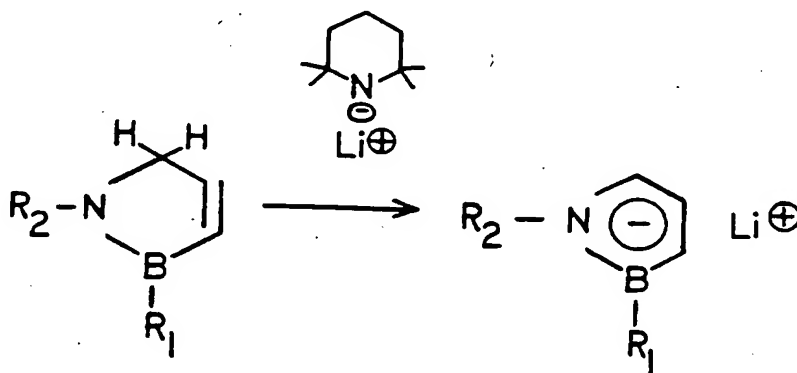
In the general formula, L_3 is an optional Lewis base. Up to an equimolar amount (with M) of base can be used. The use of the Lewis base is generally not preferred because it tends to decrease catalyst activity. However, it also tends to improve catalyst stability, so its inclusion may be desirable, depending upon the process in which the catalyst is to be used. The base may be residual solvent from the preparation of the azaboroline containing compound or it may be added separately in order to enhance the properties of the catalyst. Examples of bases that can be used in this invention include ethers such as diethylether, dibutylether, tetrahydrofuran, 1,2-dimethoxyethane, esters such as n-butylphthalate, ethylbenzoate, and ethyl p-anisate, tertiary amines such as triethylamine, and phosphines such as triethyl phosphine, tributyl phosphine, and triphenyl phosphine.

The catalysts of this invention can be prepared from commercially available starting materials. Specific starting materials that may not be commercially available can be prepared by techniques well-known in the literature as exemplified by the following. The azaboroline ligand precursor for the catalysts can be prepared from allyl amine by reacting its dianion (generated by a strong base) with an alkyl boron dihalide as described in the literature (J. Schulze, G. Schmid, J. Organomet. Chem., 193, 1980, p. 83).

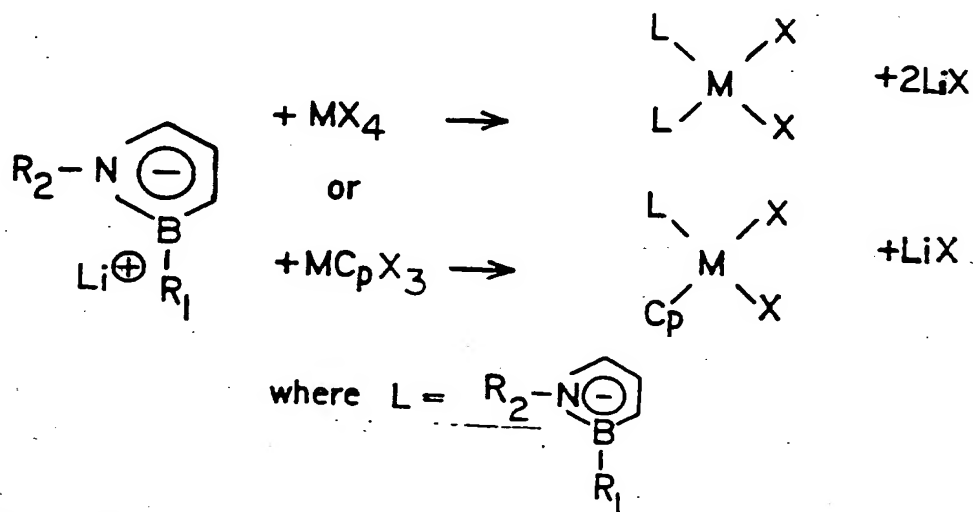


Examples of strong bases that can be used include alkyl lithium compounds such as n-butyl lithium, methyl lithium, and hydrides such as sodium hydride and potassium hydride. Two moles of base are used per mole of the allyl amine. This reaction will occur at room temperature in several hours in a hydrocarbon solvent such as pentane or hexane. Tetramethylethylenediamine in a 1:1 molar ratio with the allyl amine can be used to stabilize the alkyl lithium. The product can be isolated by vacuum and distilled to purify.

In the next step, the product is reacted with a base such as a hindered lithium reagent (e.g., lithium tetramethylpiperidide) to generate the azaborolinyllithium anion as described in the literature (G. Schmid et al., Chem. Ber., 115, 1982, p. 3830):



In the final step, the product of the second step is cooled to about -60°C and MX_4 or MCpX_3 is added. The reactants are warmed to room temperature and the reaction is complete when the reactants dissolve and LiX precipitates:



Since the catalyst is normally used in conjunction with an organometallic co-catalyst, it is preferable to dissolve the catalyst in a solvent in which the co-catalyst is also soluble. For example, if methylaluminoxane (MAO) is the co-catalyst then toluene, xylene, benzene, or ethylbenzene could be used as the solvent. Other suitable co-catalysts include aluminum alkyls having the formula $\text{AlR}'_x(\text{R}_2)_{3-x}$, where $1 \leq x \leq 3$ and R_2 is hydrogen, halide, or alkyl or alkoxide from C_1 to C_{20} , such as triethylaluminum and ethylaluminum dichloride. The preferred co-catalyst is MAO as it results in high activity and a polymer having a narrower molecular weight distribution.

The mole ratio of the organometallic co-catalyst to catalyst when used in a polymerization is generally in the range 0.01:1 to 100,000:1, and preferably ranges from 1:1 to 10,000:1.

An alternative co-catalyst is an acid salt that contains a non-coordinating inert anion (see U.S. Patent No. 5,064,802). The acid salt is generally a non-nucleophilic compound that consists of bulky ligands attached to a boron or aluminum atom, such as lithium tetrakis(pentafluorophenyl) borate, lithium tetrakis(pentafluorophenyl)aluminate, anilinium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, trityl tetrakis(pentafluorophenyl) borate, and mixtures thereof. The anion which results when these compounds react with the catalyst is believed to be weakly coordinated to the metal-containing cation. The mole ratio of acid salt to catalyst can range from about 0.01:1 to about 1000:1, but is preferably about 1:1 to 10:1. While there is no limitation on the method of preparing an active catalyst system from the catalyst and the acid salt, preferably they are mixed in an inert solvent at temperatures in the range of about -78°C to about 150°C. They can also be mixed in the presence of monomer if desired. The acid salt can be used in combination with the organometallic cocatalysts described earlier.

5 The catalyst and co-catalyst can be used on a support
such as silica gel, alumina, silica, magnesia, or titania, but
supports are not preferred as they may leave contaminants in
the polymer. However, a support may be required depending
upon the process being utilized. For example, a support is
generally needed in gas phase polymerization processes and
slurry polymerization processes in order to control the
particle size of the polymer being produced and in order to
prevent fouling of the reactor walls. The support may also
10 increase the thermal stability of the catalyst. To use a
support, the catalyst and co-catalyst are dissolved in the
solvent and are precipitated onto the support material by, for
example, evaporating the solvent. The co-catalyst can also be
deposited on the support or it can be introduced into the
15 reactor separately from the supported catalyst.

Once the catalyst has been prepared it should be used as
promptly as possible as it may lose some activity during
storage. Storage of the catalyst should be at a low
temperature, such as -100 to about 20°C. The catalyst is used
20 in a conventional manner in the polymerization of olefinic
hydrocarbon monomers. While unsaturated monomers such as
styrene can be polymerized using the catalysts of this
invention, it is particularly useful for polymerizing α -
olefins such as propylene, 1-butylene, 1-hexene, 1-octene, and
25 especially ethylene.

The catalyst is also useful in a conventional manner for copolymerizing mixtures of unsaturated monomers such as ethylene, propylene, 1-butene, 1-hexene, 1-octene, and the like; mixtures of ethylene and di-olefins such as 1,3-butadiene, 1,4-hexadiene, 1,5-hexadiene, and the like; and mixtures of ethylene and unsaturated comonomers such as norbornene, ethylidene norbornene, vinyl norbornene, norbornadiene, and the like.

The catalysts of this invention can be utilized in a variety of different polymerization processes. They can be utilized in a liquid phase polymerization process (slurry, solution, suspension, bulk phase, or a combination of these), in a high pressure fluid phase, or in a gas phase polymerization process. The processes can be used in series or as individual single processes. The pressure in the polymerization reaction zones can range from about 15 psia to about 50,000 psia and the temperature can range from about -100°C to about 300°C.

The following examples further illustrate this invention.

EXAMPLE 1

Preparation of Bis(1-tert-butyl-2-methyl- η^5 -1,2-azaboroliny)zirconium dichloride and 1-tert-butyl-2-methyl- η^5 -1,2-azaboroliny)zirconium trichloride

2-Methyl-1-tert-butyl-1,2-azaborolinyllithium was prepared by adding a solution of 0.438 g (3.2 mmol) of 2-

5 methyl-1-tert-butyl- Δ^3 -1,2-azaboroline (prepared according to
the literature procedure: J. Schultze and G. Schmid, J.
Organomet. Chem., 1980, 193, 83-91) in 6 mL of dry THF to a
cold (-78°C) solution of lithium 2,2,6,6-tetramethylpiperidide
10 (3.2 mmol) which had been prepared by reaction of equimolar
amounts of 2,2,6,6-tetramethylpiperidine and n-
butyllithium/hexanes in 10 mL THF. The cold bath was allowed
to warm up to 10°C over 1.5 hours after which the solvents
were removed under vacuum. The yellow oily residue was
15 treated with 35 mL toluene to give a yellow slurry. This was
cooled to -60°C and zirconium (IV) chloride (0.37 g, 1.6 mmol)
was added with good stirring. The bath was warmed to room
temperature and the mixture stirred overnight. The solvent
was evaporated under vacuum and residue was treated with 30 mL
20 toluene and lithium chloride filtered off. The toluene
filtrate was concentrated and the sticky yellow residue was
extracted with hexane (2 X 15 mL) and filtered. Evaporation
of hexane filtrate gave 0.14 g of a yellow solid. ¹H NMR
spectrum of the material showed it to be a ca. 2/3 mixture of
the two desired compounds.

EXAMPLE 2Preparation of (η^5 -cyclopentadienyl)(1-tert-butyl-2-methyl- η^5 -1,2-azaborolinyllithium)zirconium dichlorideMETHOD A

5 A solution of 2-methyl-1-tert-butyl-1,2-azaborolinyllithium prepared from 2-methyl-1-tert-butyl- Δ^3 -1,2-azaboroline (0.49 g, 3.5 mmol) in 20 mL THF as described above, was added dropwise via syringe to a stirred cold (-35°C) solution of cyclopentadienylzirconium trichloride
10 (0.93 g, 3.52 mmol) in 50 mL THF. The bath was allowed to warm to room temperature and the mixture stirred overnight. The solvents were evaporated in vacuo and residue extracted with 35 mL toluene and filtered. The precipitate was washed with 10 mL toluene and the combined filtrate was evaporated.
15 The resulting gummy residue was stirred with 25 mL dry hexane which produced a beige solid and a pale yellow supernatant. The mixture was filtered and the solid dried to give 0.77 g of product as a tan-colored amorphous powder. ^1H NMR spectrum of the material indicated it to be desired product contaminated
20 with some impurities.

METHOD B

2-Methyl-1-tert-butyl-1,2-azaborolinyllithium was prepared by adding a solution of 0.438 g (3.2 mmol) of 2-methyl-1-tert-butyl- Δ^3 -1,2-azaboroline (prepared according to

the literature procedure: J. Schultze and G. Schmid, J. Organomet. Chem., 1980, 193, 83-91) in 10 mL of dry toluene to a cold (-78°C) solution of lithium 2,2,6,6-tetramethylpiperidide (3.2 mmol; prepared by reaction of equimolar amounts of 2,2,6,6-tetramethylpiperidine and n-butyllithium/hexanes in 15 mL THF). The solvents were evaporated in vacuo to one-third the initial volume, the solution was cooled to -78°C and 35 mL dry toluene was added. The clear yellow solution was stirred well while cyclopentadienylzirconium trichloride (0.84 g, 3.2 mmol) was added via transfer tube. The bath was warmed to room temperature and stirred overnight. The reaction mixture was filtered, and filtrate evaporated to dryness. To the solid residue was added 20 mL toluene and the mixture was filtered to remove a dark insoluble material from a yellow filtrate. The filtrate was concentrated to give 0.34 g of a yellow amorphous powder whose ¹H NMR spectrum indicated it to be the desired product.

EXAMPLES 3 to 11

Polymerization of Ethylene With Azaborolinylyl zirconium Catalysts

The ethylene was polymerized using the catalyst prepared according to Method 2A. The polymerizations were conducted in a stirred 1.7 liter autoclave at 80 to 110°C. Dry, oxygen-

free toluene (840 ml) was charged to a clean, dry, oxygen-free reactor. MAO from Ethyl Corporation (10 wt% in toluene) was used in the polymerizations. The desired amount of MAO to give the ratio shown in the table which follows was added by syringe at 30°C. The reactor was heated to the desired temperature and sufficient ethylene was added to bring the reactor pressure to 150 psig. The reactor was allowed to equilibrate at the desired temperature and pressure. A solution of catalyst was prepared by dissolving 0.100 grams of product in 100 ml of toluene. The co-catalyst was injected into the reactor first and the catalyst was injected separately. The amount of this solution needed to give the amount of catalyst shown in the table was used to start a polymerization. Ethylene flowed into the reactor as needed in order to keep the pressure constant at 150 psig as polymer was produced.

At the end of 1 hour (less, if the activity was very high) the ethylene flow was stopped and the reactor was rapidly cooled to room temperature. The reactor was opened and the polymer was filtered from the toluene. The product was dried overnight in a vacuum oven and weighed. Table 1 gives the reaction conditions and Table 2 gives the results of polymerizations.

TABLE 1

Example	Catalyst Amount (mmoles)	MAO Amount (mmoles)	Al/TM	T(°C)	H ₂ Amount (mmoles)	Butene Amount (ml)	Run Time (hr)
3	0.00552	9.0	1630	80	0	0	0.5
4	0.00138	2.25	1630	80	0	0	0.5
5	0.00138	4.5	3261	80	0	0	0.5
6	0.00138	4.5	3261	80	30	0	1
7	0.00138	4.5	3261	80	30	20	1
8	0.00276	4.5	1630	110	0	0	1
9	0.00276	9	3261	110	0	0	1
10	0.00276	9	3261	110	30	0	1
11	0.00276	9	3261	110	30	20	1

TABLE 2

Example	Polymer Wt (g)	Productivity (kg/g Zr/hr)	M12 (dg/min)	MFR	Density (g/ml)	Mw/Mn
3	61.8	245	0.16	17.0	0.9577	-
4	42.2	670	0.03	24.2	0.9500	-
5	43.2	686	0.04	21.3	0.9529	1.79
6	71.2	566	4.29	28.7	0.9669	-
7	85.4	678	3.44	25.9	0.9503	5.14
8	62.2	247	0.92	22.1	0.9589	-
9	67.3	267	1.40	15.1	0.9622	1.74
10	80.5	320	3.56	21.7	0.9660	-
11	93.7	372	11.56	21.7	0.9483	3.73

The above table shows that polymers having a wide range of molecular weights can be made using the catalysts of this invention because the catalysts are more sensitive to hydrogen.

The melt index of the polymer was measured according to ASTM D-1238, Condition E and Condition F. MI2 is the melt index measured with a 2.16 kg weight (Condition E). MI20 is the melt index measured with a 21.6 kg weight (Condition F). MFR is the ratio of MI20 to MI2. The polymer density was measured according to ASTM D-1505. The molecular weight distribution of the polymer was measured using a Waters 150C gel permeation chromatograph at 135°C with 1,2,4-trichlorobenzene as the solvent. Both weight average molecular weight (M_w) and ratio of M_w to M_n (number average molecular weight) were used to characterize the molecular weight distribution.

EXAMPLES 12 and 13

Solution polymerizations were conducted in a stirred 2.0 liter stainless steel autoclave at 150°C. 1.0 liter of dry, oxygen-free Isopar® G (from Exxon Chemical Company) was charged to the clean, dry, oxygen-free reactor. The reactor was then allowed to equilibrate at 150°C. It was pressured with sufficient ethylene to give an ethylene partial pressure of 150 psig. No hydrogen or co-monomer were added. A solution of catalyst described in Example 2 was mixed with a solution containing 10% methylaluminumoxane (MAO) in toluene (from Albemarle Corporation and used without further purification). This mixture was stirred for 15 minutes. 10.0

5 ml of this mixture was injected into the reactor to start the polymerization. The amount of catalyst and MAO in the 10.0 ml is shown in Table 3 along with the experimental conditions. Ethylene was fed to the reactor in order to keep the pressure constant.

10 At the end of 15 minutes the ethylene flow was stopped and the reaction mixture was transferred to a vessel containing a solution of an antioxidant in Isopar® G. The solution was cooled to room temperature overnight. The polymer was filtered from the solvent by vacuum filtration. It was dried overnight in a vacuum oven and weighed. The weight of the polymer was 12.1 grams. The polymer MI2 was 118 dg/min. Additional polymer properties are shown in Table 2.

EXAMPLES 14 to 18

15 Slurry polymerization were conducted in a manner identical to that described in Examples 3 through 11. The catalyst described in Example 1 was used in those polymerizations. The polymerization conditions are shown in Table 3. The properties of the polymers which were produced
20 are shown in Table 4.

TABLE 3

Example	Catalyst Amount (mmoles)	MAO Amount (mmoles)	Al/TiN	T(°C)	H ₂ Amount (mmoles)	Butene Amount (ml)	Run Time (hr)
12	0.0138	7.5	543	150	0	0	0.25
13	0.0138	3.8	272	150	0	0	0.25
14	0.00552	9.0	1630	80	0	0	1.0
15	0.00552	13.5	2446	80	0	0	1.0
16	0.00552	13.5	2446	110	0	0	1.0
17	0.00552	13.5	2446	110	30	0	1.0
18	0.00552	13.5	2446	110	30	20	1.0

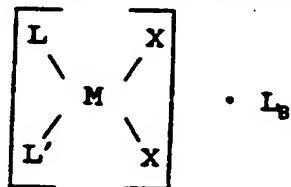
TABLE 4

Example	Polymer Wt (g)	Productivity (kg/g Zr/hr)	MI2 (dg/min)	MFR	Density (g/ml)
12	12.1	38	118	23	0.9660
13	8.8	28	108	25	0.9483
14	50.9	101	0.04	18.3	0.9609
15	49.0	97	0.06	15.0	0.9714
16	39.7	79	203	-	>0.9700
17	34.0	68	111	24.9	>0.9700
18	42.2	84	166	16.7	>0.9700

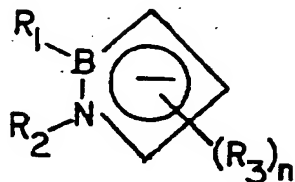
The above table shows that the catalyst has good activity and can produce polymer with very high crystallinity and density. The low MFR values indicate that the polymer has a narrow molecular weight distribution.

WE CLAIM:

1. A catalyst having the general formula

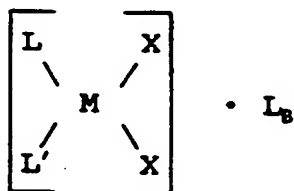


where L is a ligand having the formula

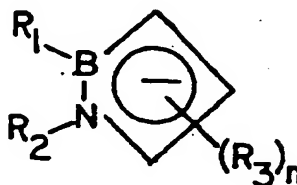


L' is L, Cp, Cp', indenyl, fluorenyl, NR₂, OR, or halogen, L can be bridged to L; X is halogen, NR₂, OR, or alkyl from C₁ to C₁₂, M is zirconium or hafnium, R is alkyl from C₁ to C₁₂ or aryl from C₆ to C₁₂, R₁ is R, alkaryl from C₆ to C₁₂, aralkyl from C₆ to C₁₂, hydrogen, or Si(R)₃, R₂ is R₁, halogen, COR, COOR, SOR, or SOOR, R₃ is R₂, OR, N(R)₂, SR, or a fused ring system, Cp is cyclopentadienyl, Cp' is pentamethylcyclopentadienyl, n is 0 to 3, and L_b is an optional Lewis base.

2. A catalyst according to Claim 1 wherein L' is Cp, Cp', or L, X is chlorine, M is zirconium, R is alkyl from C₁ to C₄, R₁ is alkyl from C₃ to C₁₂ or aryl, R₂ is t-butyl or trimethylsilyl, and R₃ is hydrogen or methyl.
3. A catalyst according to Claim 1 which is bis(1-tert-butyl-2-methyl-η⁵-1,2-azaborolynyl)zirconium dichloride.
4. A catalyst according to Claim 1 which is 1-tert-butyl-2-methyl-η⁵-1,2-azaborolynyl)zirconium trichloride.
5. A method of making a poly-α-olefin comprising polymerizing an α-olefin monomer using a catalyst that has the general formula



where L is a ligand having the formula

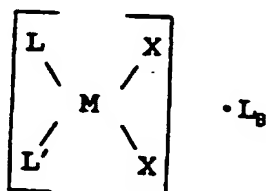


L' is L, Cp, Cp', indenyl, fluorenyl, NR₂, OR, or halogen, L can be bridged to L; X is halogen, NR₂, OR, or alkyl from C₁ to C₁₂, M is zirconium, titanium, or hafnium, R is alkyl from C₁ to C₁₂ or aryl from C₆ to C₁₂, R₁ is R, alkaryl from C₆ to C₁₂, aralkyl from C₆ to C₁₂, hydrogen, or Si(R)₃, R₂ is R₁, halogen, COR, COOR, SOR, or SOOR, R₃ is R₂, OR, N(R)₂, SR, or a fused ring system, Cp is cyclopentadienyl, Cp' is pentamethylcyclopentadienyl, n is 0 to 3, and L₃ is an optional Lewis base.

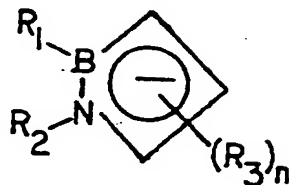
6. A method according to Claim 5 wherein L' is Cp, Cp', or L.
7. A method according to Claim 5 wherein X is halogen.
8. A method according to Claim 7 wherein X is chlorine.
9. A method according to Claim 5 wherein M is zirconium.
10. A method according to Claim 5 wherein R is alkyl from C₁ to C₄.
11. A method according to Claim 5 wherein R₁ is alkyl from C₃ to C₁₂ or aryl.

12. A method according to Claim 5 wherein R_2 is t-butyl or trimethylsilyl.
13. A method according to Claim 5 wherein R_3 is hydrogen or methyl.
14. A method according to Claim 5 wherein said catalyst is used with about 0.01 to about 100,000 moles of an organometallic cocatalyst per mole of said catalyst.
15. A method according to Claim 14 wherein said organometallic cocatalyst is methylaluminoxane.
16. A method according to Claim 5 wherein said catalyst is used with about 0.01 to about 1000 moles of an acid salt that contains a non-coordinating inert anion per mole of said catalyst.
17. A method according to Claim 16 wherein said acid salt is selected from the group consisting of lithium tetrakis(pentafluorophenyl) borate, lithium tetrakis(pentafluorophenyl) aluminate, anilinium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, trityl tetrakis(pentafluorophenyl) borate, and mixtures thereof.

18. A method of making a poly- α -olefin comprising polymerizing an α -olefin monomer using a catalyst that has the general formula



where L is a ligand having the formula



L' is L, Cp, or Cp*, L can be bridged to L, X is chlorine, M is zirconium, R is alkyl from C₁ to C₄, R₁ is alkyl from C₃ to C₁₂ or aryl, R₂ is t-butyl or trimethylsilyl, R₃ is hydrogen or methyl, Cp is cyclopentadienyl, Cp* is pentamethylcyclopentadienyl, n is 0 to 3, and L_b is an optional Lewis base.

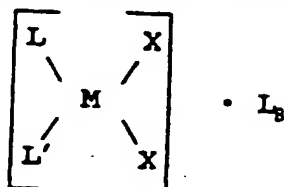
19. A method according to Claim 18 wherein said catalyst is bis(1-tert-butyl-2-methyl- η^5 -1,2-azaborolinenyl)zirconium dichloride.

20. A method according to Claim 18 wherein said catalyst is 1-tert-butyl-2-methyl- η^5 -1,2-azaboroliny)zirconium trichloride.

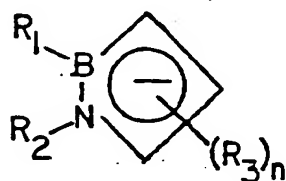
AMENDED CLAIMS

[received by the International Bureau on 30 September 1996 (30.09.96);
original claims 1, 2, 4-6, 12 and 18 amended; new claims 21-23 added;
remaining claims unchanged (7 pages)]

1. A catalyst having the general formula

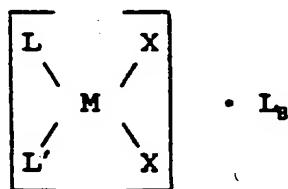


where L is a ligand having the formula

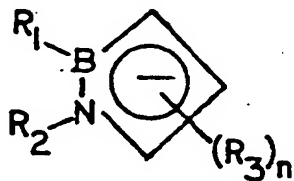


L' is cyclopentadienyl, pentamethylcyclopentadienyl, indenyl, fluorenyl, NR₂, OR, or halogen, L' can be bridged to L; X is halogen, NR₂, OR, or alkyl from C₁ to C₁₂, M is titanium, zirconium, or hafnium, R is alkyl from C₁ to C₁₂ or aryl from C₆ to C₁₂, R₁ is R, Si(R)₃, or R₄, R₄ is alkaryl from C₆ to C₁₂, aralkyl from C₆ to C₁₂, or hydrogen, R₂ is R, R₄, halogen, COR, COOR, SOR, or SOOR, R₃ is R₂, Si(R)₃, OR, N(R)₂, SR, or a fused ring system, n is 0 to 3, and L_B is an optional Lewis base.

- 1 2. A catalyst according to Claim 1 wherein L' is
 2 cyclopentadienyl or pentamethylcyclopentadienyl, X is
 3 chlorine, M is zirconium, R is alkyl from C₁ to C₄, R₁ is
 4 alkyl from C₃ to C₁₂ or aryl, R₂ is t-butyl, and R₃ is
 5 hydrogen or methyl.
3. A catalyst according to Claim 1 which is bis(1-tert-
 butyl-2-methyl-η⁵-1,2-azaborolynyl)zirconium dichloride.
4. A catalyst according to Claim 1 which is (1-tert-butyl-2-
 methyl-η⁵-1,2-azaborolynyl)zirconium trichloride.
- 1 5. A method of making a poly-α-olefin comprising
 2 polymerizing an α-olefin monomer using a catalyst that
 3 has the general formula



4 where L is a ligand having the formula

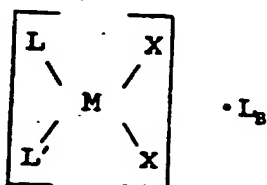


11 L' is cyclopentadienyl, pentamethylcyclopentadienyl,
12 indenyl, fluorenyl, NR₂, OR, or halogen, L' can be bridged
13 to L; X is halogen, NR₂, OR, or alkyl from C₁ to C₁₂, M is
14 zirconium, titanium, or hafnium, R is alkyl from C₁ to C₁₂
15 or aryl from C₆ to C₁₂, R₁ is R, Si(R)₃, or R₄, R₄ is
16 alkaryl from C₆ to C₁₂, aralkyl from C₆ to C₁₂, or
17 hydrogen, R₂ is R, R₄, halogen, COR, COOR, SOR, or SOOR,
18 R₃ is R₂, Si(R)₃, OR, N(R)₂, SR, or a fused ring system,
19 n is 0 to 3, and L₂ is an optional Lewis base.

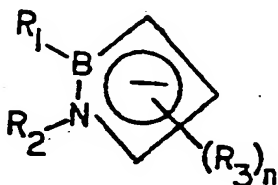
6. A method according to Claim 5 wherein L' is cyclopentadienyl or pentamethylcyclopentadienyl.
7. A method according to Claim 5 wherein X is halogen.
8. A method according to Claim 7 wherein X is chlorine.
9. A method according to Claim 5 wherein M is zirconium.
10. A method according to Claim 5 wherein R is alkyl from C₁ to C₄.
11. A method according to Claim 5 wherein R₁ is alkyl from C₃ to C₁₂ or aryl.

12. A method according to Claim 5 wherein R_2 is t-butyl.
13. A method according to Claim 5 wherein R_3 is hydrogen or methyl.
14. A method according to Claim 5 wherein said catalyst is used with about 0.01 to about 100,000 moles of an organometallic cocatalyst per mole of said catalyst.
15. A method according to Claim 14 wherein said organometallic cocatalyst is methylaluminumoxane.
16. A method according to Claim 5 wherein said catalyst is used with about 0.01 to about 1000 moles of an acid salt that contains a non-coordinating inert anion per mole of said catalyst.
17. A method according to Claim 16 wherein said acid salt is selected from the group consisting of lithium tetrakis(pentafluorophenyl) borate, lithium tetrakis(pentafluorophenyl) aluminate, anilinium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, trityl tetrakis(pentafluorophenyl) borate, and mixtures thereof.

18. A method of making a poly- α -olefin comprising polymerizing an α -olefin monomer using a catalyst that has the general formula



where L is a ligand having the formula



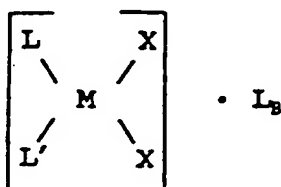
L' is cyclopentadienyl or pentamethylcyclopentadienyl, L' can be bridged to L, X is chlorine, M is zirconium, R is alkyl from C₁ to C₄, R₁ is alkyl from C₃ to C₁₂ or aryl, R₂ is t-butyl, R₃ is hydrogen or methyl, n is 0 to 3, and L₃ is an optional Lewis base.

19. A method according to Claim 18 wherein said catalyst is bis(1-tert-butyl-2-methyl- η^5 -1,2-azaborolinyl)zirconium dichloride.

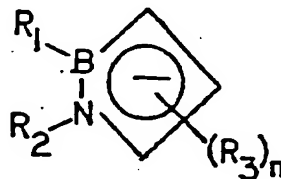
20. A method according to Claim 18 wherein said catalyst is (1-tert-butyl-2-methyl- η^5 -1,2-azaborolynyl) zirconium trichloride.

21. A catalyst according to Claim 1 wherein M is zirconium.

22. A catalyst having the general formula

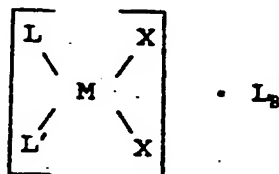


where L is a ligand having the formula

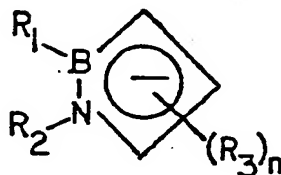


L' is L, cyclopentadienyl, pentamethylcyclopentadienyl, indenyl, fluorenyl, NR_2 , OR, or halogen, L can be bridged to L', X is NR_2 , OR, or alkyl from C_1 to C_{12} , M is titanium, zirconium, or hafnium, R is alkyl from C_1 to C_{12} or aryl from C_6 to C_{12} , R_1 is R, alkaryl from C_6 to C_{12} , aralkyl from C_6 to C_{12} , hydrogen, or $Si(R)_3$, R_2 is R_1 , halogen, COR, COOR, SOR, or SOOR, R_3 is R_2 , OR, $N(R)_2$, SR, or a fused ring system, n is 0 to 3, and L_B is an optional Lewis base.

23. A catalyst having the general formula



where L is a ligand having the formula



L' is L, cyclopentadienyl, pentamethylcyclopentadienyl, indenyl, fluorenyl, NR₂, OR, or halogen, L can be bridged to L', X is halogen, NR₂, OR, or alkyl from C₁ to C₁₂, M is titanium, zirconium, or hafnium, R is alkyl from C₁ to C₁₂ or aryl from C₆ to C₁₂, R₁ is a C₆ to C₁₂ aryl group, a C₆ to C₁₂ alkaryl group, a C₆ to C₁₂ aralkyl group, hydrogen, or Si(R)₃, R₂ is R₁, a C₁ to C₁₂ alkyl group, halogen, COR, COOR, SOR, or SOOR, R₃ is R₂, OR, N(R)₂, SR, or a fused ring system, n is 0 to 3, and L₃ is an optional Lewis base.

INTERNATIONAL SEARCH REPORT

Interns 1 Application No

PCT/US 96/03665

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F10/00 C07F17/00 B01J31/18 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C07F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 590 486 (IDEMITSU) 6 April 1994 see page 4, line 55 - page 5, line 3 see claims 1,3	1,3, 5-10, 12-19
X	see page 7, line 51 - line 53	14
X	see page 12; table 1	15-17
P,X	JP,A,07 258 322 (IDEMITSU) 9 October 1995 see abstract	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

2 July 1996

Date of mailing of the international search report

30.07.96

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Authorized officer

Fischer, B

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/US 96/03665

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-590486	06-04-94	JP-A- 6340704	13-12-94
JP-A-7258322	09-10-95	NONE	